Sborník vědeckých prací Vysoké školy báňské – Technické univerzity Ostrava
číslo 1, rok 2009, ročník LII, řada hutnická
článek č. 1451

THE INFLUENCE OF THE ADHESION OF PROMOTERS ON THE BASED CARBOXYLATES OF TRANSITION METALS ON PROPERTIES OF RUBBER COMPOUNDS

M. PAJTÁŠOVÁ*, D. ONDRUŠOVÁ, E. JÓNA, S. ĽALÍKOVÁ, T. BAZYLÁKOVÁ, V. PETRÁŠOVÁ

Faculty of Industrial Technologies, Department of Inorganic Materials and Environmental Engineering, Alexander Dubček University of Trenčín; Púchov, Slovak Republic, contact author: pajtasova@fpt.tnuni.sk

ABSTRACT: This work is devoted to the study of rubber additives on the base of carboxylates of transition metals and it studies their influence on the physical and mechanical properties and rubber-steel-cord adhesion for passenger car tyres. The influence of the adhesive on vulcanization process and the bonding mechanism between separate chains, as well as their bonding to the brass substrate is very complicated and it is not completely interpreted in spite of tremendous number of works devoted to this problem. Therefore the experimental testing of the adhesion quality between rubber and brass-coated steel cord remains the main criterion for evaluating the acceptance of new adhesion promoters. An appraisal of the values of adhesion between rubber and brass-coated steel cord obtained in standard tearing tests show that synthesized adhesion promoters based on cobalt carboxylates achieve adhesion values comparable to those achieved by commercial promoter of adhesion.

KEY WORDS: carboxylates of transition metals, adhesion, rubber to steel cord, physical and mechanical properties

1. INTRODUCTION

One of the basic criteria influencing the properties of passenger car tyres is the adhesion of the rubberizing compound to the brass-coated steel cord. In order to achieve a high degree of rubber to metal adhesion, it is necessary to use important group of substances known as adhesion promoters. Carboxylate complexes with transition metals have proved successful for the rubber to steel cord system [1,2].

Apart from some disadvantages, systems based on Co(II) complexes possess quite a number of advantages, for example: they ensure an excellent initial adhesion to metals; they improve adhesion to steel with no surface treatment and hence ensure adhesion on the cut joints of the steel-cord used in tyres; they reduce the processing problems [3,4].

Chandra and co-workers have carried out systematic investigations of the influence of cobalt promoters on the adhesion energy and curing reactions and they assumed that Co(II) ion forms a chelate complex with the accelerator and its fragments [4,5].

2. EXPERIMENT

All M(II) carboxylate complexes were prepared in the reaction between heated aqueous solution of sodium salt of the corresponding carboxylic acid with the heated aqueous solution of Co(II) or Zn(II) sulphate:

$$R\text{-}COOH + NaOH \rightarrow R\text{-}COONa + H_2O$$

$$2\ R\text{-}COONa + M(SO_4) \rightarrow (R\text{-}COO)_2M + Na_2SO_4$$

where M(II) = Co, Zn.

Three newly modified compounds were prepared with the addition of three new adhesion promoters (CO14, CP2, ZN16) and they were compared to the reference rubber compound with adhesion promoter – manobond C680 (MA). The quality of the rubber compounds with additions of adhesion promoters based on Co(II) or Zn(II) carboxylate complexes was evaluated in tests according to Sk-La50-029 (static test before age), STN 62 1522 (after age) and STN 62 1464 (dynamic test - Henley) – and the determination of adhesion to the steel cord type OK 2 x 0,30 HT, for passenger car tyres. Adhesion is determined by the method of tearing steel cord from the rubber. We used the Instron 4302 equipment with the head force range of 5 kN and Zwick 1101 equipment with the head force range of 1 kN.

Vulcanization characteristics were tested and physical-mechanical properties of newly prepared systems were studied. Determination of vulcanization characteristics was made by vulcameter Monsanto 100 by STN 62 1416 at the temperature of 150 °C during 60 min. For determination of physical-mechanical properties of vulcanized rubber – stress-strain properties (Tensile strength, Modulus 300, Elongation) was made by instrument INSTRON at the temperature of 23 ± 2 °C by STN 62 1436. Hardness was measured by hardness tester IRHD by STN 62 1433 at the temperature of 23 ± 2 °C.

3. RESULTS AND DISCUSSION

Results of adhesion properties of study rubber compounds are given in Tables 1, 2 and in Figs. 1 and 2.

Tab. 1: The values of adhesion – static test before age and after age

Compound	Adhesion - static test [N/10mm]	Standard deviation	Adhesion- after age [N/10mm]	Standard deviation
MA	364	26.8	348	26.8
CO14	372	22.3	362	23.2
CP2	364	20.5	355	19.7
ZN16	239	22.5	206	11.9

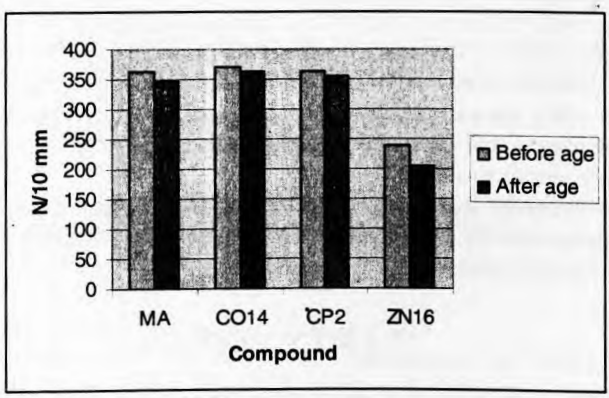

Fig. 1: The adhesion static tests according to Sk-La50-029 and STN 62 1522

Tab. 2: The values of adhesion – method of Henley

Compound	Adhesion method of Henley [N/10mm]		Adhesion method of Henley after age [N/10mm]	
	static test	dynamic test	static test	dynamic test
MA	281	235	274	231
CO14	216	214	258	223
CP2	296	282	268	260
ZN16	252	211	221	188

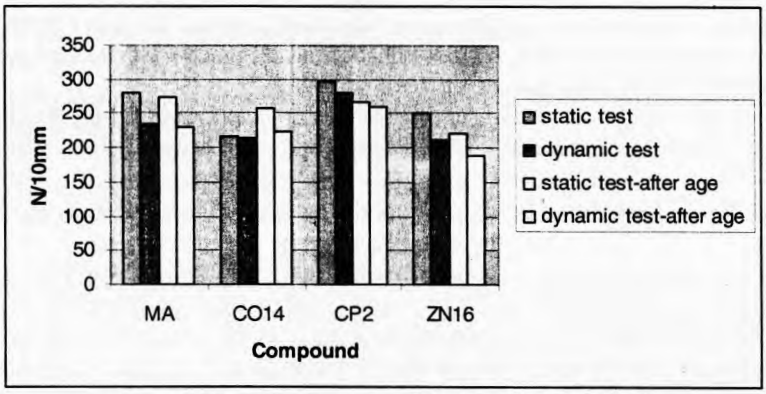

Fig. 2: The adhesion test of Henley STN 62 1464

The values of adhesion between rubber compounds containing Co(II) carboxylate complexes (CO14 and CP2) and steel cord of type OK 2 x 0,30 HT are comparable or higher to those containing MA. The values of adhesion between rubber compounds containing Zn(II) carboxylate complex (ZN16) and steel cord of type OK 2 x 0,30 HT are lower than those containing manobond C 680 (MA).

Processing and vulcanization properties of rubber compounds are given in Table 3 and physical and mechanical properties are given in Tables 4, 5.

Tab. 3: Processing and vulcanization properties of rubber compounds

Compound	Mooney viscosity 100 °C, 1+4 [ML]	Mooney Safety 120 °C [min]	Optimum of cure 150 °C [min]	T point 95 MDR 2000 [min]
MA	67.7	33.22	25	19.97
CP2	67.8	31.73	25	20.59
CO14	64.6	30.76	25	21.68
ZN16	61.5	33.77	30	26.05

Tab. 4: Physical and mechanical properties of studied compounds before age

Compound	Tensile strength [MPa]	Modulus 300 [MPa]	Hardness [Sh A]	Elasticity [%]	Elongation [%]
MA	23.99	15.46	72	35	457
CP2	23.76	15.69	71	36	443
CO14	21.48	13.63	70.5	35.5	437
ZN16	23.89	15.49	69	37	444

Tab. 5: Physical and mechanical properties of studied compounds after age (100 °C/ 72 h)

Compound	Tensile strength [MPa]	Modulus 200 [MPa]	Hardness [Sh A]	Elongation [%]
MA	21.64	15.94	80	288
CP2	18.8	14.32	78.5	266
CO14	20.42	19.15	78	329
ZN16	20.0	14.1	76	286

In the course of vulcanization, a stable bond is formed between the brass layer and the rubber compound. With the progressing time of vulcanization, at a constant temperature and pressure, the volume of free sulphur decreases and the volume of bonded sulphur increases.

The values of processing and vulcanization characteristics and physical-mechanical properties of newly prepared rubber compounds are comparable with the properties of commercial rubber compound.

4. CONCLUSION

In three newly prepared rubber compounds was commercial promoter of adhesion – manobond C 680 (MA) substituted by new adhesion promoters on the basis of carboxylate complexes with Zn(II) or Co(II). Vulcanization characteristics and physical properties of newly prepared systems were compared to the properties of commercial rubber compound for passenger car tyres containing manobond.

An appraisal of the values of adhesion between rubber and steel cord contained in Tab. 1 and Tab. 2 shows that synthesized adhesion promoters based on Co(II) carboxylate complexes (CO14, and CP2) achieve adhesion values comparable to those achieved with manobond C 680 (MA), which is currently used, and that the sythesized promoters positively influence the initial value of adhesion between rubber and steel cord. On the other hand, values of adhesion of rubber compound containing Zn(II) carboxylate complex (ZN16) are below the minimal value of adhesion in passenger car tyres.

Acknowledgements: The authors sincerely thank the Slovak Grant Agency VEGA 1/3161/06 and AV 4/2014/08 for the financial support.

5. REFERENCES

[1] PAJTÁŠOVÁ, M., ONDRUŠOVÁ, D., JÓNA, E., ĎURIŠ, Š.: *Plasty a kaučuk*, 35, 1998, 103.
[2] CHANDRA, A. K. et al.: *Kautschuk Gummi Kunststofe*, 50, 1997, 106.
[3] VAN OOIJ, W. J: *Rubb. Chem. Technol.*, 57, 1984, 421.
[4] CHANDRA , K. et al.: *KGK*, 50, 1997, 106.
[5] JÓNA, E., PAJTÁŠOVÁ, M., ONDRUŠOVÁ, D., ŠIMON, P.: *J. Anal. Appl. Pyrol.*, 63, 2002, 17.